

Kramers-like picture for crystal nucleation

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We introduce a new scheme to analyze the kinetics of homogeneous nucleation in terms of a global order parameter. Our approach is based on the application of the internal degrees of freedom formalism¹ to derive a kinetic equation of the Kramers type formulated for a global reaction coordinate. We provide explicit expressions for the quantities and coefficients involved in the process, suitable for simulation. In addition, our picture recovers in the quasi-stationary case the transition rate obtained from the method of reactive flux. The equation we present may provide a link between theoretical approaches to homogeneous nucleation (generally formulated in terms of a kinetic equation of the Fokker-Planck type) and simulations (which mostly employ linear response theory). In this context, our scheme provides a theoretical framework to interpret and extend the results obtained in recent simulations.²⁻⁴

I. INTRODUCTION

Nucleation is the fundamental mechanism of many phase transformations, and has been the subject of extensive theoretical and experimental investigations.⁵ In the last years, computer simulations have also become a useful tool to study the kinetics of crystal nucleation. However, in order to analyze the results of simulations the most common theoretical treatments for nucleation processes are not generally employed.

The kinetics of homogeneous nucleation is habitually described from a theoretical point of view by means of kinetic equations of the Fokker-Planck type focused on the size distribution of the clusters present in the system. These equations are formally analogous to the ones arising from Kramers reaction-rate theory,^{6,7} since in fact nucleation is an activated process. The several approaches proposed to evaluate nucleation rates differ basically in the expressions for the drift and diffusion coefficients of the Fokker-Planck equation. The values of these coefficients are sometimes postulated, assumed as unspecified parameters, or left in terms of the addition and loss rates of one monomer to a cluster. To estimate these rates a proper microscopic kinetic model is required. These theories are customarily used to evaluate steady-state nucleation rates, and most of them assume the constancy of the diffusion coefficient.

Contrarily, two different ways to proceed exist for simulations. On the one hand, there is a type of simulation,⁸ which can be called "straightforward", whose method consist of simply supercooling the system and then waiting for the appearance of nuclei. Since the nucleation barrier decreases as $1/(\Delta T)^2$, where ΔT is the degree of supercooling, this type of simulation based on observing the spontaneous formation of nuclei requires experimentally inaccessible supercoolings. For more moderate and realistic conditions the nucleation barrier is so large that a spontaneous crossing is extremely unlikely during the typical times of a simulation.

Recently, a different type of simulation, allowing the study of nucleation under more realistic undercoolings, has been introduced by ten Wolde, Ruiz-Montero and Frenkel in refs. 2-4. Their method is based on the separation of the simulation into two parts: the evaluation of the nucleation barrier following the Van Duijneveldt-Frenkel scheme⁹ and the subsequent calculation of the nucleation rate by means of the Bennett-Chandler picture,¹⁰⁻¹² based on linear response theory. The macroscopic state of the simulated system is described by means of a reaction coordinate connecting the initial and final phases and sensitive to the global degree of crystallinity in the system. Concretely, Frenkel and co-workers use a set of bond-order parameters introduced by Steinhardt *et al.*¹³

One may wonder why they use linear response theory instead of appealing to the usual nucleation theories or even to the prototypical theory of activated processes: the Kramers theory. In fact, in their simulations^{2,3} they report on a diffusive behavior that seems to corroborate the validity of Kramers picture. Additionally, they also employ Kramers equation in order to obtain reasonable estimates of the time evolution of the system.

In reference 14 the authors themselves give the reasons why they do not use Kramers theory. First, they assert that it was originally formulated for the single particle diffusion problem and therefore its validity is not guaranteed in the case when the reaction coordinate is a global one. On the other hand, they point out that the diffusion coefficient, assumed to be constant in Kramers picture, may depend on the value of the reaction coordinate, and moreover its expression may be non-trivial. Finally, they affirm that a Fokker-Planck description of nucleation processes does not take into account hydrodynamic effects that may be very important in this type of barrier-crossing processes.

Our purpose in this paper is to introduce a theoretical description of homogeneous nucleation in terms of a global order parameter like the one used by Frenkel and co-workers in their simulations. The treatment we present is based on the kinetic equation introduced in a previous paper¹⁵ and derived from the application of the internal degrees of freedom formalism.^{1,16} We want to show how the scheme we propose provides a complete description of the process, it includes the transition rate expression of the method of reactive flux as a quasi-stationary limit, and it overcomes the reservations exposed by Frenkel *et al.*

The paper is structured as follows. In section II, we outline and briefly review the method of reactive flux from which expressions used by Frenkel's group in their simulations are derived. In section III, we introduce and extend the internal degrees of freedom formalism to the situation where the internal coordinate is a non-local order parameter. Within this framework, we derive a Kramers-like equation, which in section IV is particularized to the quasi-stationary case to prove that it recovers the results of the method of reactive flux. In section V, we describe the way to proceed beyond the quasi-stationary limit. Finally, in the last section we summarize and comment on the main results of the theory we propose.

II. METHOD OF REACTIVE FLUX.

Our aim in this section is to present a brief review of the derivation, the limitations, and the scope of applicability of the method of reactive flux to evaluate reaction rates. To this end, let us consider a macroscopic system whose state is characterized by a reaction coordinate Q . This system can be in two different states, A and B , separated by an energy barrier whose maximum is located at position Q_0 . The state of the system, i.e. the side of the barrier where it is located, can be characterized by the functions

$$n_A(t) = \theta[Q_0 - Q(t)] \quad (1)$$

$$n_B(t) = \theta[Q(t) - Q_0] \quad (2)$$

where θ is the step function, and $n_A(t)$, $n_B(t)$ obviously satisfy the condition

$$n_A(t) + n_B(t) = 1 \quad (3)$$

The probability that our system is in state A at time t will be given by the non-equilibrium average of the characteristic function $n_A(t)$

$$P_A(t) = \langle n_A(t) \rangle \quad (4)$$

The starting point of this theory is to postulate the validity of the following phenomenological equation describing the dynamics of the populations in states A and B

$$\frac{dP_A(t)}{dt} = k_{BA}P_B(t) - k_{AB}P_A(t) \quad (5)$$

where $P_B(t) = 1 - P_A(t)$, and k_{AB} and k_{BA} are the forward and backward rates, respectively. These rates are assumed to be constant and satisfy the detailed balance condition

$$\frac{k_{AB}}{k_{BA}} = \frac{P_B^{eq}}{P_A^{eq}} \quad (6)$$

In the spirit of Onsager's regression hypothesis, we assume that the relaxation of $\Delta P_A(t) \equiv P_A(t) - P_A^{eq}$ from an initial non-equilibrium deviation $\Delta P_A(0)$ follows the same exponential decay as the equilibrium correlation function of the fluctuations

$$\frac{\Delta P_A(t)}{\Delta P_A(0)} = \frac{\langle \Delta n_A(0) \Delta n_A(t) \rangle_{eq}}{\langle \Delta n_A(0) \Delta n_A(0) \rangle_{eq}} = e^{-\lambda t} \quad (7)$$

where $\Delta n_A(t) = n_A(t) - \langle n_A \rangle_{eq}$, the symbol $\langle \dots \rangle_{eq}$ represents an equilibrium average, and the relaxation rate λ is given by

$$\lambda = k_{AB} + k_{BA} \quad (8)$$

From these equations one can obtain the following formula for the transition rate, employed by ten Wolde, Ruiz-Montero and Frenkel in their simulations²⁻⁴

$$k_{AB} = \frac{\langle \dot{n}_B(0)n_B(t) \rangle_{eq}}{\langle n_A \rangle_{eq}} = \frac{\langle \dot{Q}(0)\delta[Q(0) - Q_0]\theta[Q(t) - Q_0] \rangle_{eq}}{\langle n_A \rangle_{eq}} \quad (9)$$

This expression is not valid for very short times (because the relaxation of the system cannot be exponential at $t = 0$). Additionally, it is also restricted to times t satisfying the condition $t \ll 1/\lambda$, since during the derivation it is assumed that $e^{-\lambda t} \approx 1$. Moreover, we notice that although k_{AB} is a time independent rate, in expression (9) it is equated to a correlation function depending explicitly on time. Therefore, the latter equation is only correct for times long enough that the correlations have reached a plateau value.

On the other hand, taking into account the identity

$$n_B(t) - n_B(0) = \int_0^t dt' \frac{dn_B(t')}{dt'} \quad (10)$$

and since the equilibrium average $\langle \dot{n}_B n_B(0) \rangle_{eq}$ vanishes, one can rewrite eq. (9) as follows

$$k_{AB} = \int_0^t \frac{\langle \dot{n}_B(0)\dot{n}_B(t') \rangle_{eq}}{\langle n_A \rangle_{eq}} dt' \quad (11)$$

As asserted before, this expression is only valid for times long enough that the correlations have achieved a plateau. For such values of the time, it is then meaningful to assume that the velocity autocorrelation function has decayed to zero, so that we can replace the upper limit of the previous integral by infinity. Therefore, the final expression for the transition rate yields

$$k_{AB} = \frac{1}{\langle n_A \rangle_{eq}} \int_0^\infty \langle \dot{n}_B(0)\dot{n}_B(t) \rangle_{eq} dt = \frac{1}{\langle n_A \rangle_{eq}} \int_0^\infty \langle \dot{Q}(0)\delta[Q(0) - Q_0]\dot{n}_B(t) \rangle_{eq} dt \quad (12)$$

This expression will be recovered by using the treatment we introduce in the next section.

III. NON-EQUILIBRIUM THERMODYNAMICS APPROACH. INTERNAL DEGREES OF FREEDOM

The key element of the approach we propose is the formulation of a kinetic equation to describe homogeneous nucleation in terms of the order parameter Q characterizing the global degree of crystallinity of the system. This equation has already been introduced in a previous paper,¹⁵ and we will devote this section to an extended and complete derivation of this equation. The procedure is based on the application of the internal degrees of freedom formalism, which constitutes a straightforward method to obtain kinetic equations for any adequate internal coordinate or degree of freedom of the system. In particular, we use this formalism considering Q as the system internal coordinate.

Until now, in all of previous papers where this formalism has been successfully applied,^{1,16-21} the system was always described by means of a local internal coordinate identifying each system constituent independently. As a result, a Kramers-like equation was obtained. However, we are now interested in a kinetic description in terms of a single global order parameter Q , characterizing the whole system. Therefore, we need to extend the internal degrees of freedom formalism to allow a description in terms of a global internal coordinate. In fact, we face the same problem pointed out by Frenkel and co-workers¹⁴ about the validity and the necessity of an extension of Kramers picture when the reaction coordinate is a global one.

From the point of view adopted in previous papers,¹⁶⁻²¹ one worked with a system of N identical particles. The internal coordinate characterized the state of each particle, which evolved independently without interacting with the remaining particles. The global state of the system was obtained at each instant by means of a statistical recount of the individual states of the N particles.

In our case, however, we are interested in a contracted description of the system based on a single internal coordinate that characterizes it in a global way. Proceeding by analogy, we consider N system replicas, identical in the sense that all of them are compatible with a given macroscopic state (identified for example by the total number of particles, the pressure, and the temperature). This set of replicas constitutes a non-equilibrium ensemble, defining the "system" we are going to deal with. Since we are working with an ensemble, we will be able to relate and obtain statistically the properties of a single replica from the behavior of the whole ensemble. Denoting the probability density by $\rho(Q, t)$, the quantity $\rho(Q, t)dQ$ represents the fraction of replicas with a value of the degree of crystallinity between $(Q, Q + dQ)$,

at the instant t . For N large enough, the latter expression could be interpreted as the probability that a single replica of the ensemble has a value of the internal coordinate between $(Q, Q + dQ)$.

Therefore, the value of a quantity A evaluated for a single replica could be assimilated with the expected value of this observable in the non-equilibrium ensemble characterized by $\rho(Q, t)$. That is

$$A(t)|_{\text{replica}} \Longleftrightarrow \langle A(t) \rangle_{\text{ensemble}} = \int_{Q_1}^{Q_2} A\rho(Q, t)dQ \quad (13)$$

Again, in order to derive our kinetic equation, our starting point will be the Gibbs equation for the entropy variation associated with a diffusion process through the energy barrier that separates the states Q_1 (the value of the order parameter in the metastable phase) and Q_2 (corresponding to the new stable phase)

$$\delta S = -\frac{1}{T} \int_{Q_1}^{Q_2} \mu(Q, t) \delta \rho(Q, t) dQ \quad (14)$$

Here δS is the variation of entropy per replica, T is the temperature (taken as constant) and $\mu(Q, t)$ is the conjugate chemical potential. The latter equation corresponds to the variation of entropy in a diffusion process, with the assumption that the internal energy and the volume of the system are constant.

It is worth pointing out that the Gibbs equation constitutes a reformulation of the Gibbs entropy postulate. Indeed, from the fact that we are working with system replicas that obviously do not interact with each other, the expression for the chemical potential is that for an ideal system

$$\mu(Q, t) = k_B T \ln \rho(Q, t) + \Phi(Q) \quad (15)$$

where $\Phi(Q)$ is the energy barrier to be surpassed by a replica in order to achieve the new stable phase. Bearing in mind that at equilibrium the chemical potential becomes constant, the following expression for the energy barrier could be obtained from the latter equation

$$\Phi(Q) = \mu_{eq} - k_B T \ln \rho_{eq}(Q) \quad (16)$$

Therefore, we can rewrite the chemical potential as follows

$$\mu(Q, t) = \mu_{eq} + k_B T \ln \frac{\rho(Q, t)}{\rho_{eq}(Q)} \quad (17)$$

Substitution of this equation in expression (14) yields

$$\delta S = -k_B \int \delta \rho(Q, t) \ln \frac{\rho}{\rho_{eq}} dQ \quad (18)$$

which is just the expression for the variation of the entropy obtained from the Gibbs entropy postulate. Consequently, the equation we use as starting point in our derivation, namely eq. (14), constitutes an alternative formulation of the Gibbs entropy postulate more proper for a non-equilibrium thermodynamics description. Therefore, it essentially represents the variation of S with respect to its local equilibrium value in terms of the distribution over the possible internal states associated with different values of the order parameter Q .

The evolution of the number density $\rho(Q, t)$ is governed by the continuity equation

$$\frac{\partial \rho(Q, t)}{\partial t} = -\frac{\partial J(Q, t)}{\partial Q} \quad (19)$$

where $J(Q, t)$ is the diffusion current in the internal space. From eq. (14) we can obtain the entropy production associated with this diffusion process

$$\sigma = -\frac{1}{T} \int J(Q) \frac{\partial \mu(Q)}{\partial Q} dQ \quad (20)$$

where we have employed eq. (19) and a partial integration has been performed, assuming vanishing flux at initial and final states.

The entropy production (20) has the usual form of a sum of flux-force pairs. Following the non-equilibrium thermodynamics method, we may formulate the phenomenological equation

$$J(Q, t) = -\frac{L(Q)}{T} \frac{\partial \mu(Q, t)}{\partial Q} \quad (21)$$

where $L(Q)$ is the phenomenological coefficient, which may in general depend on the internal coordinate. To derive this expression, locality in the internal space has been assumed, for which only fluxes and forces with the same value of the internal coordinate are coupled.

By substituting (21) in (19) and using eq. (15) for the chemical potential, we obtain the following kinetic equation in the internal space

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial Q} \left(D(Q, t) \frac{\partial \rho}{\partial Q} + b(Q, t) \frac{\partial \Phi}{\partial Q} \rho \right) \quad (22)$$

where

$$b(Q, t) = \frac{L(Q)}{\rho(Q, t)T} \quad (23)$$

and

$$D(Q, t) = k_B T b(Q, t) \quad (24)$$

are the mobility and the diffusion coefficient in the internal space, respectively.

Equation (22) characterizes the evolution of the non-equilibrium physical ensemble, determining in a complete way the nucleation process in terms of the global order parameter Q . In order to fully specify this equation, we need an expression for the barrier $\Phi(Q)$ and for the phenomenological coefficient $L(Q)$ relating the flux and its conjugate force in the internal space.

The value of the energy barrier is given by eq. (16), and could be evaluated by means of simulations. In fact, this type of simulations for global order parameters involved in nucleation processes has already been performed by van Duijneveldt and Frenkel.⁹

On the other hand, to obtain an explicit expression for the phenomenological coefficient $L(Q)$, we will adopt the fluctuating hydrodynamics framework.²⁰ From this point of view, one considers that the total current in the internal space is the result of two contributions: a systematic part J^s and a random term J^r including the fluctuations inherent in the diffusion process along the internal coordinate. One has

$$J(Q, t) = J^s(Q, t) + J^r(Q, t) \quad (25)$$

We will assume that J^r has zero mean and satisfies the fluctuation-dissipation theorem

$$\langle J^r(Q, t) J^r(Q', t') \rangle = 2k_B L(Q) \delta(Q - Q') \delta(t - t') \quad (26)$$

Finally, from the latter equation one can derive the following Green-Kubo expression for the phenomenological coefficient

$$L(Q) = \frac{1}{k_B} \int_{Q_1}^{Q_2} dQ' \int_0^\infty dt \langle J^r(Q', 0) J^r(Q, t) \rangle \quad (27)$$

The objective of the two following sections will be to transform this expression into a formula suitable for computer simulations. First, we consider the quasi-stationary case to show how to recover explicitly the method of reactive flux expression commonly used to evaluate nucleation rates. Subsequently, we will analyze the general case.

IV. THE TRANSITION RATE FOR THE QUASI-STATIONARY CASE.

When the supercooling or the supersaturation is low enough, the energy barrier to surpass in the nucleation process is large compared with thermal energy. In this high barrier situation, the system achieves a quasi-stationary state characterized by a uniform current

$$J(Q, t) = J(t) \{ \theta(Q - Q_1) - \theta(Q - Q_2) \} \quad (28)$$

and a chemical potential which equilibrates independently at each side of the barrier

$$\mu(Q, t) = \mu(Q_1, t)\theta(Q_0 - Q) + \mu(Q_2, t)\theta(Q - Q_0) , \quad (29)$$

where Q_0 represents the position of the top of the barrier and θ is the step function. By substituting this equation in (15) one obtains the following expression for the probability density

$$\rho(Q, t) = \rho(Q_1, t)e^{-\frac{\Phi(Q)-\Phi(Q_1)}{k_B T}}\theta(Q_0 - Q) + \rho(Q_2, t)e^{-\frac{\Phi(Q)-\Phi(Q_2)}{k_B T}}\theta(Q - Q_0) \quad (30)$$

On the other hand, the diffusive current can be written in a more convenient way as

$$J(Q, t) = -D(Q, t)e^{-\Phi/k_B T} \frac{\partial}{\partial Q} e^{\mu/k_B T} \quad (31)$$

By equating (31) and (28), and by integrating over Q with the help of eq. (29), one arrives at the following expression for the nucleation rate

$$J(t) = \frac{D(Q_0)}{Q_2 - Q_1} e^{-\Phi_0/k_B T} \left(e^{\mu_1/k_B T} - e^{\mu_2/k_B T} \right) \quad (32)$$

where the subindexes 0, 1 and 2 indicate that the corresponding function is evaluated at Q_0 , Q_1 and Q_2 , respectively.

Having obtained the nucleation rate expression for the quasi-stationary case, our goal now will be to show that it is equivalent to the method of reactive flux equation derived from linear response theory. An important difference between our formalism and the method followed in the simulations is that we are working with a non-equilibrium ensemble of replicas, while in simulations one makes reference to a single system or a single replica. The connecting point that links our scheme with the results referred to a single system is the probabilistic interpretation of the ensemble number density $\rho(Q, t)$.

Bearing this probabilistic interpretation in mind, we will see how to recover the transition rate expression (12). The first step will be to transform the continuity equation into the phenomenological starting equation of the method of reactive flux. By integrating eq. (19) from Q_1 to Q_0 , and using the quasi-stationary condition (28) and the result (32) one obtains

$$\frac{d}{dt} \int_{Q_1}^{Q_0} \rho(Q, t) dQ = -J(t) = \frac{D(Q_0)}{Q_2 - Q_1} e^{-\Phi_0/k_B T} \left(e^{\mu_2/k_B T} - e^{\mu_1/k_B T} \right) \quad (33)$$

where $\int_{Q_1}^{Q_0} \rho(Q, t) dQ = P_A(t)$ is just the probability that the system would be on the left hand side of the barrier, at time t .

From (23) and (24) the diffusion coefficient expression at the top of the barrier is given by

$$D(Q_0, t) = \frac{k_B L(Q_0)}{\rho(Q_0, t)} \quad (34)$$

By using (15) and (30), the density $\rho(Q_0, t)$ could alternatively be expressed as

$$\rho(Q_0, t) = e^{\mu_1/k_B T} e^{-\Phi_0/k_B T} \quad (35)$$

On the other hand, from eq. (30) and (15) it follows

$$e^{\mu_2/k_B T} = \rho_2 e^{\Phi_2/k_B T} = \frac{\int_{Q_0}^{Q_2} \rho(Q, t) dQ}{\int_{Q_0}^{Q_2} e^{-\Phi/k_B T} dQ} = \frac{P_B}{\int_{Q_0}^{Q_2} e^{-\Phi/k_B T} dQ} \quad (36)$$

Here P_B represents the probability of being on the right hand side of the barrier. By introducing these two latter expressions into eq. (33), one arrives at

$$\frac{dP_A(t)}{dt} = k_{BA}(t)P_B(t) - k_{AB}(t)P_A(t) \quad (37)$$

where

$$k_{AB}(t) = \frac{L(Q_0)k_B}{(Q_2 - Q_1)P_A(t)} \quad (38)$$

and

$$k_{BA}(t) = \frac{L(Q_0)k_B}{(Q_2 - Q_1)P_A(t)} \frac{\int_{Q_1}^{Q_0} e^{-\Phi/k_B T} dQ}{\int_{Q_0}^{Q_2} e^{-\Phi/k_B T} dQ} \quad (39)$$

are the forward and backward rates, respectively.

Therefore, we have just obtained the equation governing the evolution of the probability that the system would be on the metastable side of the barrier. At this point, we have to highlight two important differences with respect to the method of reactive flux. First, we have obtained this equation as a particular case (corresponding to a quasi-stationary situation) of a more general theory of wider applicability. Moreover, the rate coefficients in our expression are explicitly time-dependent, which does not happen in the formula of the method of reactive flux. Finally, it is important to remark that our rate coefficients fulfill the detailed balance condition

$$\frac{k_{AB}(t)}{k_{BA}(t)} = \frac{P_B^{eq}}{P_A^{eq}} \quad (40)$$

as follows from eqs. (16), (38) and (39). This condition guarantees that the flux vanishes at equilibrium.

The last task to carry out is to compare the rate $k_{AB}(t)$ with the reactive flux formula (12). Within that framework, the expression (9) is identified with the rate k_{AB} at times large enough so that the correlations have achieved a stable value characterized by a plateau. In our expression, for long times the probability P_A will approach and can be replaced by the equilibrium value $P_A^{eq} = \langle n_A \rangle_{eq}$, and therefore k_{AB} will become time independent.

On the other hand, the random component J^r of the current is related to the fluctuations of P_A with respect to the equilibrium value. Indeed, by integrating the continuity equation (19) from Q_1 to Q one obtains

$$\frac{\partial N(Q, t)}{\partial t} = -J(Q, t) = -J^s(Q, t) - J^r(Q, t) \quad (41)$$

where

$$N(Q, t) = \int_{Q_1}^Q \rho(Q', t) dQ' \quad (42)$$

Notice that eq. (41) is valid for arbitrary times. In a very short time scale -microscopic time scale²²- we can write

$$\frac{\partial \delta N(Q, t)}{\partial t} = -J^r(Q, t) \quad (43)$$

where the time derivative $\frac{\partial \delta N(Q, t)}{\partial t}$ is the instantaneous rate of change.²³ Therefore

$$\langle J^r(Q', 0) J^r(Q, t) \rangle_{eq} = \left\langle \frac{\partial \delta N(Q', 0)}{\partial t} \frac{\partial \delta N(Q, t)}{\partial t} \right\rangle_{eq} \quad (44)$$

with $\delta N = N - N_{eq}$. In the quasi-stationary state, described by eq. (28), the quantity $\frac{\partial \delta N(Q', t)}{\partial t}$ is independent of the position Q' of the absorbing barrier. Hence, we can particularize for convenience the latter expression for $Q' = Q_0$, and taking into account that

$$\frac{d \delta N(Q_0, t)}{dt} = \frac{d}{dt} \langle \Delta n_A(t) \rangle = -\frac{d}{dt} \langle \Delta n_B(t) \rangle \quad (45)$$

we can then rewrite the phenomenological coefficient (27) as

$$k_B L(Q_0) = (Q_2 - Q_1) \int_0^\infty dt \langle \langle \dot{n}_B(0) \rangle \langle \dot{n}_B(t) \rangle \rangle_{eq} \quad (46)$$

Finally, substitution of this expression in eq. (38) yields

$$k_{AB} = \frac{1}{\langle n_A \rangle_{eq}} \int_0^\infty dt \langle \langle \dot{n}_B(0) \rangle \langle \dot{n}_B(t) \rangle \rangle_{eq} \quad (47)$$

By remembering the link between ensemble averages and the values associated with a single system, the equivalence between this equation and expression (12) is then obviously proven.

V. GENERAL CASE

The method of reactive flux used by Frenkel and co-workers in their simulations considers that the barrier separates the system into two states, A and B , and it is restricted to the evaluation of the transition rate between these initial and final states. In particular, it provides no information about the evolution of the intermediate configurations. In the previous section, we have proven that this scheme corresponds to a quasi-stationary case associated with high nucleation barriers. The theory we propose also allows us to evaluate the evolution and the time-dependent rate of change of the global crystallinity Q of the system, at any intermediate state between Q_1 and Q_2 .

Our scheme is formulated in terms of a Kramers-like equation accounting for the evolution of $\rho(Q, t)$. From the knowledge of the number density $\rho(Q, t)$ one could then evaluate the relevant quantities of the system.

In the general case, one must work with the kinetic equation (22) which constitutes the central point of our approach. This equation contains the free energy barrier $\Phi(Q)$ and the phenomenological coefficient in the internal space $L(Q)$. The barrier $\Phi(Q)$ could be evaluated from simulations analogous to the ones performed in reference 9. In section III we have obtained an explicit expression for the coefficient $L(Q)$. However, it is necessary to transform eq. (27) into an expression more proper for simulations.

With the help of eq. (43), one can relate the rate of change of the order parameter to the random contribution to the current in the following way

$$\langle \dot{Q}(t) \rangle = \int_{Q_1}^{Q_2} Q \frac{\partial \delta \rho(Q, t)}{\partial t} dQ = \int_{Q_1}^{Q_2} J^r(Q, t) dQ \quad (48)$$

By substitution of the latter expression and eq. (43) into the Green-Kubo formula (27) for $L(\gamma)$ (where γ represents an arbitrary value of the degree of crystallization) we finally obtain

$$k_B L(\gamma) = - \int_0^\infty dt \langle \dot{Q}(0) \delta \dot{N}(\gamma, t) \rangle_{eq} \quad (49)$$

In the equation above there appears the expected value $\langle \dot{Q}(0) \rangle$, which could be identified with the initial speed of change $\dot{Q}(0)$ of the system which is being simulated. Additionally, the term $\delta \dot{N}(\gamma, t)$ is given by

$$\delta \dot{N}(\gamma, t) = - \langle \dot{n}_\gamma(t) \rangle \quad (50)$$

where $n_\gamma(t) = \theta[Q(t) - \gamma]$.

With these considerations in mind, the definitive expression in a form suitable for simulation yields

$$L(\gamma) = \frac{1}{k_B} \int_0^\infty dt \langle \dot{Q}(0) \dot{n}_\gamma(t) \rangle_{eq} \quad (51)$$

Note that the latter equation for the phenomenological coefficient is formally similar to expression (12), analyzed in sections II and IV. However, two significant differences exist. The first difference comes from the fact that in eq. (12), the only trajectories giving a non-vanishing contribution are the ones corresponding to configurations initially at the top of the barrier. The second consists of the replacement of the characteristic function $n_B(t) = \theta[Q(t) - Q_0]$ of eq. (12) for $n_\gamma(t)$. Therefore, by performing simulations analogous to the ones carried out by Frenkel and co-workers, we could obtain the phenomenological coefficient $L(\gamma)$ for any value γ of the degree of crystallization. Knowing $L(\gamma)$, since the barrier $\Phi(Q)$ could be evaluated from simulations, we could completely determine the Kramers-like eq. (22). By solving this equation we could determine the probability density $\rho(Q, t)$ describing the dynamics of the system.

VI. CONCLUSIONS

In this paper we have introduced a systematic scheme to treat homogeneous nucleation, applicable to any type of global order parameters describing the process. This scheme is based on the internal degrees of freedom formalism inside the framework of non-equilibrium thermodynamics. In fact, we have provided an extension of this formalism to allow descriptions in terms of order parameters, relying on the construction of a non-equilibrium ensemble.

Our treatment links theory with simulations, in the sense that the equation we propose is a Kramers-like equation as the ones commonly used at the theoretical level, but its coefficients are susceptible to be determined from simulations. Moreover, it constitutes a unifying proposal where the expressions of the method of reactive flux emerge in the quasi-stationary limit of a more general Kramers-type theory.

The approach we have introduced provides a complete and fully consistent description of homogeneous nucleation for an order parameter such as the one used by Frenkel and co-workers in their simulations. Our scheme not only includes the reactive flux theory, but also it allows a deeper study of the process, offering a framework for a theoretical interpretation of simulation results. We have outlined that by performing simulations analogous to the ones carried out in the quasi-stationary case, one could in principle obtain more complete information about the process. For example, we could study time-dependent nucleation and follow the evolution and the rate of change of intermediates degrees of crystallinity Q .

Additionally, our scheme casts light on the drawbacks exposed by Frenkel *et al.* Our picture overcomes the first objection, in the sense that our equation constitutes the proof of the validity of a Kramers-like diffusive equation for global order parameters. The equation we propose also takes into account the possible dependences on Q and even on t of the diffusion coefficient. Moreover, it gives explicit expressions to evaluate it, which in fact are very similar to the ones used by Frenkel and co-workers in their simulations.

Finally, with respect to their last concern we have to remark that the fact of working with a global description, where one characterizes the macroscopic state of the system by means of a single coordinate, implies that hydrodynamic effects, that are of local character, cannot be taken into account. However, by employing a local description of the process (like the one used in ref. 15), the formalism we have introduced enables us to study hydrodynamic effects in nucleation processes. In order to analyze these effects, we must increase the number of variables to achieve a more detailed description of the system, and consider additional contributions in the Gibbs eq. (14). The way to proceed has been outlined in references 17 and 18 and will be applied to nucleation processes in a future contribution.

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BIBLIOGRAPHY

1. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, (Dover, New York, 1984).
2. P. R. ten Wolde, M. J. Ruiz-Montero and D. Frenkel. J. Chem. Phys. **104**, 9932 (1996).
3. P. R. ten Wolde, M. J. Ruiz-Montero and D. Frenkel. Faraday Discuss. **104**, 93 (1996).
4. P. R. ten Wolde, M. J. Ruiz-Montero and D. Frenkel. Phys. Rev. Lett. **75**, 2714 (1995).
5. Some reviews on nucleation: a) K. F. Kelton. Solid State Phys. **45**, 75 (1991). b) D. T. Wu. Solid State Phys. **50**, 37 (1996). c) A. C. Zettlemoyer. *Nucleation*. (Marcel Dekker, New York, 1969). d) A. Laaksonen, V. Talanquer and D. W. Oxtoby. Annu. Rev. Phys. Chem. **46**, 489 (1995). e) P. G. Debenedetti. *Metastable Liquids: concepts and principles*. Chap. 3. (Princeton University Press, 1996).
6. H. A. Kramers. Physica **VII**, 284 (1940).
7. P. Hänggi, P. Talkner and M. Borkovec. Rev. Mod. Phys. **62**, 251 (1990).
8. For example: a) C. S. Hsu and A. Rahman. J. Chem. Phys. **71**, 4974 (1979). b) R. D. Mountain and A. C. Brown. J. Chem. Phys. **80**, 2730 (1984). c) S. Nosé and F. Yonezawa. J. Chem. Phys. **84**, 1803 (1986). d) L. A. Báez and P. Clancy. J. Chem. Phys. **102**, 8183 (1995).
9. J. S. van Duijneveldt and D. Frenkel. J. Chem. Phys. **96**, 4655 (1992).
10. D. Chandler. J. Chem. Phys. **68**, 2959 (1978).
11. D. Chandler, *Introduction to Modern Statistical Mechanics*, (Oxford University Press, 1987).
12. C. H. Bennett, in *Algorithms for Chemical Computation*, edited by R. E. Christofferson (American Chemical Society, Washington. D. C., 1977).
13. P. J. Steinhardt, D. R. Nelson and M. Ronchetti. Phys. Rev. B **28**, 784 (1983).
14. M. J. Ruiz-Montero, D. Frenkel. and J. J. Brey. Molecular Physics **90**, 925 (1997).

15. D. Reguera, J. M. Rubí and A. Pérez-Madrid. *Physica A*, in press.
16. I. Prigogine and P. Mazur. *Physica* **XIX**, 241 (1953).
17. A. Pérez-Madrid, J. M. Rubí, and P. Mazur. *Physica A* **212**, 231 (1994).
18. J. M. Rubí and P. Mazur. *Physica A*, **250**, 253 (1998).
19. I. Pagonabarraga and J. M. Rubí. *Physica A* **188**, 553 (1992).
20. I. Pagonabarraga, A. Pérez-Madrid, J. M. Rubí. *Physica A* **237**, 205 (1997).
21. G. Gomila, A. Pérez-Madrid, J. M. Rubí. *Physica A* **233**, 208 (1996).
22. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics Vol 5* (Statistical Physics Part 1) §118 and *Vol 9* (Statistical Physics Part 2) (Pergamon Press, New York, 1980).
23. R. Zwanzig. *Annu. Rev. Phys. Chem.* **16**, 67 (1965).